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ABSTRACT

The total energy of metallic copper as a function of the atomic radius is calculated. The model assumes that in copper one has nearly free s-electrons in OPW states and d-electrons localized at the ions in atomic-like orbitals. The coulomb interactions in the energy are calculated by using the model of neutral spheres, while the kinetic and exchange contributions to the S^2-energy are approximated by the exchange charge model. Instead of the familiar Born-Mayer repulsion, which was found to lead to controversies in the case of copper, the d-type interaction energy shows a more complex behaviour having a minimum near the equilibrium atomic radius. The prediction for the cohesive energy and the equation of state is reasonable, the calculated value for the Ashcroft radius for s-electrons agrees remarkably with the 'ab initio' estimate. The atomic-like orbitals minimizing the total energy are shomewhat more extended than the real atomic wave-functions.

KIVONAT

Kiszámitottuk a réz teljes energiáját, mint az atomi térfogat függvényét. Modellünkben a réz elektronjai részben közel-szabad s elektronok, melyeket ortogonalizált sikhullámokkal irunk le, részben az ionok körül lokalizált d elektronok atomi jellegü pályákon. A Coulomb kölcsönhatásokat a semleges-gömb-modell segitségével számitottuk ki, mig a kinetikus és kicserélődési energia járulékát az S^2-es energiataghoz az "exchange charge model" felhasználásával határoztuk meg. A d tipusu kölcsönhatási energiajárulék az egyensulyi atomi térfogat közelében minimumot mutat, ellentétben a szokásos Born-Mayer taszitás exponenciális viselkedésével. A kohéziós energia értékére és az állapotegyenletre a tapasztalattal összhangban lévő eredményeket kaptunk, az 'Ashcroft sugár' értéke is jól egyezett az 'ab initio' becsléssel. Az atomi jellegü d pályák, melyek minimalizálják a teljes energiát, valamivel kiterjedtebbeknek adódtak, mint a valódi atomi hullámfüggvények.

РЕЗЮМЕ

В работе была рассчитана общая энергия меди, как функция атомного радиуса. В модели предполагалось, что в меди имеются почти свободные s-электроны в ОПВ состояниях и локализованные на ионах d-электроны на орбитах атомного типа. Кулоновский член в энергии рассчитывался в модели нейтральных сфер, а кинетический и обменный члены в S^2 энергии вычислялись с помощью модели "обменного заряда". Вместо привычного Борн-Майеровского отталкивания, приводящего к противоречиям в случае меди, энергия взаимодействия d-типа ведет себя сложнее и имеет минимум вблизи равновесного атомного радиуса. Предсказания для энергии связи и для уравнения состояния разумные. Рассчитанная величина Ашкрофтовского радиуса для s-электронов находится в хорошем согласии с рассчитанными из "первых принципов". Орбиты атомного типа, минимизирующие энергию, оказались более размазанными, чем настоящие атомные волновые функции.

1. INTRODUCTION

Since the classical work of Fuchs [1] a number of attempts have been made to clarify the nature of cohesion in noble metals, in particular, in copper. Part of these efforts were made to calculate directly the total energy as a function of lattice coordinates using more or less parametric expressions, in the hope that by use of a reasonably small set of parameters all available experimental data can be reproduced [2], [3]. The other kind of approach [4], [5], [6], [7], [8] regarded copper as a particular element of the iron transition series with the d-band filled and applied band structure theory to make predictions on cohesive properties.

In the parametric approach it is essential that the presence of d-electrons has, as a rule, been assumed to cause merely repulsion /of Born-Mayer type, for example/ between the ions, in other respects the calculation being the same as that for an alkali metal. It has turned out, however, that models of this kind are far too oversimplified, as shown occasionnally by the resulting nonphysical values of the model parameters. This has clearly indicated the need for a somewhat more realistic account of the d-states in copper, with special regard to total energy calculation. At first sight, such a theory is readily available as implicit in any suitable scheme of band structure theory by which the one-electron spectrum can be obtained. This is, however, not so for two reasons. Firstly, the knowledge of one-electron energies is only an intermediate step to obtain the so-called 'band structure contribution' to the total energy, and in the procedure of summation most of the subtle structure of the one-electron spectrum becomes, anyhow, irrelevant. Secondly, it is even more important that to obtain the total energy the absolute positions of the bands are needed relative to, say, the atomic levels, and not the structure of the bands relative to each other. Moreover, in discussing the problem of cohesion of simple metals it was found [9] [10] , that the gross features of the volume dependent total energy are essentially determined by some structure-independent quantities like the bottom of the conduction band, the average potential, etc. In fact, in the case of non-transition metals the very simple model of neutral spheres [10] was seen to give a fairly good description of the cohesive properties for a number of elements, ignoring any band structure effects, and the results of Brovman et al [11] have shown that by a similarly simple model with a single parameter one is able to explain the 'universal' equation of state for the alkalis.

The present work is intended to generalize this argument for the case of copper. The model assumes the existence of localized atomic-like states for d-electrons in the metal, which are orthogonal to each other, while the s-electrons extend into orthogonalized plane wave /OPW/ states. Electron-electron and electron - ion interactions are calculated in an analytical framework, and only two parameters are introduced, namely the Ashcroft radius for the OPW states and the amplitude of the exchange charge repulsion [12]. The main result can be interpreted as follows. The total energy consists of two parts, first an essentially s-energy contribution having a similar dependence on volume as that found by Fuchs [1], and second a specific d-type contribution, representing the effect of interaction between d-shells, which is however, by no means a simple repulsive term. On the contrary, both its value and its contribution to pressure being slightly negative, it has the character of an attractive interaction at the equilibrium lattice spacing. It is only for shorter atomic radii that this energy term becomes repulsive, having a large positive curvature at the equilibrium volume. Only this particular shape of the d-type energy makes it possible that the s-energy shows a similar dependence on the atomic radius as that of the 'ab initio' results [1], while at the same time the cohesive properties related to the total energy can be reasonably well predicted. If instead of that the d-type energy were represented by a simple Born-Mayer repulsion of the filled d-shells [2], [3], the model parameters as determined from equilibrium cohesion data would necessarily lead to a spurious contraction of the s-energy curve towards smaller atomic radii, or even to imaginary Ashcroft radius for the s-electrons. On fitting the two parameters of the model from the equilibrium lattice constant and bulk modulus values, the present model predicts the cohesive energy and the equation of state up to 5 Mbar reasonably well, while the value of the Ashcroft radius and the position of the bottom of the s-band correlate well with the theoretical expectations. An analysis of the balance between different energy components is given, the positions of the average or 'renormalized' energy levels [6] are compared with other work. In particular, the cancellation [6] between energy contributions arising from the upward shift of the one-electron d-levels and that from the change in electron-electron interaction terms is discussed, since this point seems to be important in context with some previous work [13], [14] on the cohesion in transition elements.

2.1 BASIC ASSUMPTIONS

For a metal with Z bonding electrons, the total energy per atom can be written as

$$E = E_k + E_{ec} + E_{ee} + E_{cc} \qquad /2.1/$$

where the different terms are the kinetic energy

$$E_k = \frac{1}{N} \int \left(-\nabla_r^2,\ \rho(\underline{r}\underline{r}')\right)_{\underline{r}'\to\underline{r}} d\underline{r} \qquad /2.2/$$

the electron - ion core interaction

$$E_{ec} = \frac{2}{N} \left\{ \int \frac{\rho(\underline{r})\,\rho_c(\underline{r})}{|\underline{r}-\underline{r}'|}\, d\underline{r}\, d\underline{r}' - \frac{1}{2} \int \frac{\rho(\underline{r}\underline{r}')\ \rho_c(\underline{r}'\underline{r})}{|\underline{r}-\underline{r}'|}\, d\underline{r}\, d\underline{r}' \right\} \qquad /2.3/$$

the electron - electron interaction between bonding electrons,

$$E_{ee} = \frac{1}{N} \left\{ \int \frac{\rho(\underline{r})\,\rho(\underline{r}')}{|\underline{r}-\underline{r}'|}\, d\underline{r}\, d\underline{r}' - \frac{1}{2} \int \frac{\rho(\underline{r}\underline{r}')\ \rho(\underline{r}'\underline{r})}{|\underline{r}-\underline{r}'|}\, d\underline{r}\, d\underline{r}' \right\} + U_c \qquad /2.4/$$

and the coulomb repulsion of non-overlapping spherical ion cores,

$$E_{cc} = \frac{1}{N} \sum_{L\neq L'} \frac{Z^2}{|\underline{R}_L - \underline{R}_{L'}|} \qquad /2.5/$$

Here N is the number of atoms, $\rho(\underline{r}\underline{r}')$ and $\rho_c(\underline{r}\underline{r}')$ are the real-space density matrices [15] for the bonding and core electrons, respectively, the latter assumed to be the same as for free ions, $\underline{R}_L$ is the coordinate of the L-th ion, and $\rho(\underline{r})$ and $\rho_c(\underline{r})$ are related to the diagonal elements of the density matrices as

$$\rho(\underline{r}) = \rho(\underline{r}\underline{r})$$

$$\rho_c(\underline{r}) = \rho_c(\underline{r}\underline{r}) - A \sum_L \delta(\underline{r}.\underline{R}_L)$$

where A is the atomic number of the element. Here and in the following the energy is given in rydbergs. The last term in /2.4/ is the correlation energy of bonding electrons which is added explicitly to the Hartree-Fock terms.

To evaluate these expressions, for non-transition metals the pseudopotential method is quite appropriate. In the case of noble or transition elements, however, the large overlapping d-shells make the definition of a suitable pseudopotential scheme rather difficult. Although the formalism can be generalized [5] to deal also with d-band metals, the method becomes rather complicated. The application of the model hamiltonian approach to calculate cohesive energy is also problematic, since there is apparently no way of unambiguously prescribing the dependence of the resonance parameters on the atomic volume [16].

The present approach may be termed as a nearly-free electron-tight binding approximation, the first main assumption of the model is that

i/ there are two kinds of state for the electrons in copper: Wannier-states composed purely from atomic-like d-orbitals, and nearly free s-electron states combined from orthogonalized plane wave /OPW/ functions. Non-orthogonality of these two sets of states is neglected, i.e. the OPW-s are orthogonal only to inner core orbitals.

Building up the total wavefunction as a Slater determinant of these functions, one obtains

$$\rho(\underline{r}\underline{r}') = \rho_s(\underline{r}\underline{r}') + \rho_{d,w}(\underline{r}\underline{r}') \qquad /2.6/$$

where ρ_s is the density matrix for nearly free s-electrons, of the same form as that for an alkali metal, and $\rho_{d,w}$ is the d-electron density composed from the Wannier-functions centred at the ions.
In the 'naive' approximation /which may, however, be justified, as seen below/ of taking the Wannier states as orthogonalized combinations of atomic-like functions [15] one obtains that

ii/ the density matrix is split into two parts,

$$\rho_{d,w}(\underline{r}\underline{r}') = \rho_d^o(\underline{r}\underline{r}') + \rho_d^{ov}(\underline{r}\underline{r}') \qquad /2.7/$$

where the first term contains superposed atomic-like densities composed from atomic-like d-orbitals ψ_λ

$$\rho_d^o(\underline{r}\underline{r}') = \sum_L \rho_{dL}^o(\underline{r}\underline{r}')$$

$$\rho_{dL}^o(\underline{r}\underline{r}') = 2 \sum_{\lambda=-2}^{2} \psi_\lambda^*(\underline{r}-\underline{R}_L;\alpha)\, \psi_\lambda(\underline{r}'-\underline{R}_L,\alpha) \qquad /2.8/$$

and the second term is the 'overlap density' arising from the orthogonalization. Here λ goes from -2 to 2, and α stands for a set of parameters /effective charge, etc/ which are included into the definition of ψ_λ and may take different values in the metal and the atom.

In the above approximation ρ_d^{ov} has the following properties,

a/ $\rho_d^{ov}(\underline{r}\underline{r}')$ is, in lowest order, proportional to the overlap integral S between two ψ_λ at neighbouring lattice sites,

b/ the density $\rho_d^{ov}(\underline{r})$ describes a depletion of electronic charge strongly localized midway between two ions, called the 'exchange charge', and the corresponding increase of charge elsewhere.

keeping only the lowest power of S in ρ_d^{ov} the resulting energy terms are all of order S^2. The exchange charge approximation [18], [12] makes use of this fact, and the practically point-like localization of the exchange charge, to take all terms arising from ρ_d^{ov} in the energy to be formally proportional to S^2. This will also be followed here.
The strong localization of the exchange charge implies that its effects on the energy cannot be described by a model which uses only spherically symmetric charge distributions.
On the other hand, one may try to apply the model of neutral spheres to the rest of the charge distribution described by $\rho_s(\underline{r})$ and $\rho_d^o(\underline{r})$ Thus it is assumed that

iii/ for a first approximation to the volume dependent total energy

a/ $\rho_s(\underline{r}\underline{r}')$ can be composed from free OPW-s, ignoring the coherent scattering of OPW-s in the ions, and

b/ the diagonal term of the atomic-like d-density $\rho_d^o(\underline{r})$, as defined by/2.8/, can be approximated by a sum of spherically symmetric densities $\tilde{\rho}_{dL}(\underline{r})$ defined inside the Wigner-Seitz spheres,

$$\rho_d^o(\underline{r}) = \sum_L \tilde{\rho}_{dL}(r) \qquad \tilde{\rho}_{dL}(r) = 0 \qquad r > R_{ws} \qquad /2.9/$$

Although with an appropriate construction for $\tilde{\rho}_{dL}(r)$, the above assumptions lead to a convenient framework for the total energy calculation, some points have to be clarified. First, the neglect of non-orthogonality between the OPW-s and the d-states and further, representing the nearly free electron states by single, unscattered OPW-s lead to rather a poor approximation from the point of view of the one-electron problem. We should stress here that the total energy is much less sensitive to these effects than the one-electron spectrum, and though these approximations are by far too trivial to yield a realistic band structure, they may work sensibly for the present purpose*. /The formal reason for this is that the shifts in the one-electron levels are averaged out and tend to cancel each other. In other words, the total energy contains the second power of the lattice potential in lowest order, in contrast to the first order term determining band gaps./ In fact, for simple metals with only ρ_s, the structure-independent model of neutral spheres turns out to give reasonable estimates for the cohesive properties /within 10 per cent in average/ [10] and it works particularly well for the alkalis [11]. In the case of copper, as pointed out already, the strong structure dependence of the S^2 terms in the energy makes it necessary to treat this contribution separately, and the argument is used only to the rest of the energy.

*It was shown, for example, that the total energy of the s-band electrons is but very little influenced by hybridization with d-bands [4].

Another point to question is the use of atomic-like functions for the d-electron states. The problem is that the actual resonant wavefunctions which could, in fact, be used instead of the atomic ones in constructing Wannier states in a tight binding scheme do not fall off exponentially with distance [19]. It has, however, been shown by Pettifor [20] that the long oscillating tail of the resonant wavefunction can exponentially be cut down and transformed into the OPW contribution, without affecting the one-electron eigenvalues, while the rest of the resonant state have already the shape of an 'effective' atomic orbital. The adequacy of the traditional atomic-like approach is thus clarified, defining at the same time the 'ab initio' atomic-like wavefunction for crystal energy calculation. Here this 'effective' wavefunction will be approximated by a modified atomic orbital adjusted so as to minimize the total energy*.

Finally, the exchange charge approximation to be used here differs from the original formulation [12], [18], as a consequence of assumption iii/b. According to this, the coulomb terms connected with ρ_d^o are calculated accurately within the frame of the spherical density approximation, without assuming them to be proportional to S^2.

This way of treating the coulomb terms in a closed form, without recourse to an S^2 approximation, leads to important consequences in the atomic radius dependence of the d-electron energy, called traditionally as core-core interaction.

As to the coefficient of the S^2 energy term, no attempt has been made to calculate it presently and it is left as a free parameter. This familiar procedure [12] seems to be justified by the fact that, even if one takes the LCAO approach literally /which is probably not correct for copper/ and determines this coefficient, the cancellation between different two-centre integrals [15] makes the result much uncertain.

2.2 ENERGY OF THE NEARLY FREE S-ELECTRONS

Inserting /2.6/ and /2.7/ into /2.1/ - /2.4/, the expression for the total energy is divided into a number of terms containing different combinations of ρ_s, ρ_d^o and ρ_d^{ov}. Using assumption iii on the spherically symmetric neutral atomic spheres, the interatomic coulomb terms cancel, while the interatomic exchange for d-electrons, alike terms containing ρ_d^{ov}, is seen to be of order S^2. One has

$$E = E_s + E_d \qquad /2.10/$$

where the s-energy contribution is defined as

$$E_s = \left(T_s + E_{cs} + E_{ss}\right) + E_{ds}^o \qquad /2.11/$$

while the rest of the total energy, called as d-type energy, is

*The renormalized atom by Watson et al [6] and the method of Lipari and Deegan [21] show other examples of defining localized atomic-like d-states for energy calculation purposes.

$$E_d = T_d^o + E_{cd}^o + E_{dd}^o + E_d^S \qquad /2.12/$$

In simple terms, E_s is the nearly free s-electron energy and E_d contains the interaction energy between filled d-shells. The meaning of the symbols is obvious, indices s and d refer to s and d electrons, T is kinetic energy, cs means core-s-electron interaction etc. The upper index o indicates that the quantity contains only ρ_d^o in the definition, and E_d^S is the S^2 energy arising from ρ_d^{ov} and interatomic d-exchange*. As an example, the d-s interaction has the form

$$E_{ds}^o = \int_{WS} \frac{\rho_d^o(\underline{r})\ \rho_s(\underline{r}')}{|\underline{r}-\underline{r}'|}\, d\underline{r}\, d\underline{r}' - \frac{1}{2N} \int \frac{\rho_d^o(\underline{r}\underline{r}')\ \rho_s(\underline{r}'\underline{r})}{|\underline{r}-\underline{r}'|}\, d\underline{r}\, dr'$$

where WS indicates that the integration is confined to a Wigner-Seitz sphere. The first term in bracket in /2.11/ is clearly the first order approximation to the ground state energy of a nearly free electron system embedded in the field of positive ions, with the electronic density of that for free OPW-s. The particular feature of this expression is that the term 'ion' refer to copper atoms stripped both their outer s and d electrons off. With this modification the spherical approximation to the coulomb terms within the cell gives [10]

$$E_s = \left(\frac{3}{5} k_F^2 - \frac{3z}{R_a} + \frac{3zr_i^2}{R_a^3} + \frac{1{,}2}{R_a} - \frac{0{,}916}{R_a} + U_c(R_a) \right) + E_{ds}^o(R_a) \qquad /2.13/$$

where the first term in bracket is the free-electron-like kinetic energy /k_F being the Fermi wavenumber/, the next term is the bare coulomb attraction between the core and the s-electrons, the third is the average of the non-coulombic part of electron-ion interaction defined through the parameter r_i**, while the next three terms are the coulomb, exchange and correlation energies for free electrons. The atomic or Wigner-Seitz radius is defined as

$$\frac{4\pi}{3} R_a^3 = \text{atomic volume}$$

We modify /2.13/ first by taking into account the 'orthogonality hole' at the core region and the corresponding increase of density elsewhere, which is characteristic to the OPW density. This can be done [10] by multiplying the charge z by a factor $\tilde{\lambda}$ defined as

*This definition of E_d^S differs from that by Löwdin [15] in that it includes d-d exchange and is defined without the coulomb overlap terms.

**For an Ashcroft potential r_i has the direct meaning of core radius [22]. For more general pseudopotentials [10], [11] $3r_i^2$ is still a positive quantity, though defined by more potential parameters.

$$\tilde{\lambda} = \left\{\left(1 - \sum_{c,\text{core}} |(\underline{k}|\varphi_c)|^2\right)^{-1}\right\}_{av}$$

where φ_c -s are inner core orbitals and the summation goes over the core states, $(\underline{k}|$ represents a plane wave state, and the expression in bracket is to be averaged over all $\underline{k}$ values. For the present calculation the simplified expression

$$\lambda_o = \left(1 - \sum_{s,\text{core}} |(o|\varphi_s)|^2\right)^{-1} \qquad /2.14/$$

may be used, where the notation shows explicitly that for $\underline{k} = 0$ only matrix elements for inner s-states survive. The error in replacing $\tilde{\lambda}$ by λ_o is fairly small, as shown by the example in Kleinmann's paper [23], because at a general $\underline{k}$ the decrease in $|(\underline{k}|\varphi_s)|^2$ from $|(\underline{k}|\varphi_p)|^2$ is almost compensated by terms like $|(\underline{k}|\varphi_p)|^2$ making the average close to λ_o. The dependence of λ_o /and of $\tilde{\lambda}$ / on the atomic radius is particularly simple, namely

$$\lambda_o = \left[1 - (r_c/R_a)^3\right]^{-1} \qquad r_c^3 = \sum_{s,\text{core}} \left|\int \varphi_s \, dr\right|^2 \qquad /2.15/$$

The length r_c may be called the 'OPW core radius', and by definition it is an atomic quantity. One can expect intuitively that the final value of the parameter r_i should be not far from this 'ab initio' core radius, if a model expression like /2.13/ has any meaning. This will be seen indeed the case here.

Introducing then the orthogonality hole correction to /2.13/ and regrouping the terms gives

$$E_s = E_{s,b}(R_a) + \frac{2{,}21\lambda_o}{R_a^2} + \frac{0{,}284}{R_a} + U_c(R_a) \qquad /2.16/$$

where the expression

$$E_{s,b}(R_a) = z\lambda_o\left(-\frac{3}{R_a} + \frac{3r_i^2}{R_a^3}\right) + E_{ds}^o(R_a) \qquad /2.17/$$

has a physical meaning in itself, as shown below. In addition to multiplying the ionic charge by λ_o, the same enhancement factor has been applied to the free-electron type kinetic energy to obtain /2.16/ from /2.13/.

By this one simply takes into account the stretching of the free band, as caused by the energy dependence of the psudopotential [10]. For the correlation energy the Nozieres-Pines expression

$$U_c(R_a) = -0{,}115 + 0{,}031 \ln R_a$$

has been employed.

Returning now to the quantity $E_{s,b}$ one can see that for $z\lambda_o = 1$ and neglecting E^o_{ds} it becomes the Fröhlich - Bardeen expression for the lowest lying s-state energy /the bottom of s-band/ in a one-valency metal [24]. Although the physical meaning of r_i as a core radius, as mentioned above, is only qualitative, it can nevertheless be defined precisely by using the conditions of lattice equilibrium. It is rather remarkable that r_i as defined by the lattice equilibrium condition [11] reproduces the lowest band energy as calculated by direct band structure methods [25] for sodium and potassium, within 5-10 per cent of accuracy. In the case of copper the Bardeen-Fröhlich expression applies only to the cores without d-electrons, and the d-s interaction must be treated as different from the interaction of s electrons with inner core states. This is necessary, since at a variation of R_a, the ρ^o_d d-electron density itself changes. Postponing for the moment the calculation of E^o_{ds} to a later stage, one can still transform formally equ. /2.17/ to the form

$$E_{s,b} = \lambda_o \, z_{eff}(R_a) \left(- \frac{3}{R_a} + \frac{3r_i^2}{R_a^3} \right) \qquad /2.18/$$

with r_i^2 adjusted from lattice equilibrium and the function $z_{eff}(R_a)$ is defined unambiguously by the dependence of E^o_{ds} on R_a. Since intuitively one expects that the main effect of E^o_{ds} is to screen out most of the ionic charge connected with stripping the d-electrons off the core, z_{eff} must be near to unity. It will be seen that z_{eff} is, in fact, remarkably constant within a large range of R_a. It is more important, however, that /2.17/ or equivalently /2.18/ can be interpreted as the bottom of the s-band in copper, as seen by comparing /2.16/ and /2.17/, just in the same way as for, say, potassium, and accordingly one expects the error to be no more than 10 per cent.

The most important result of this section is, therefore, that the s-electron energy can, similarly to the case of a simple one-valency metal, be specified by a single free parameter r_i^2 which, in turn, must be determined from the dynamical equilibrium of the lattice. The unique difference from the simple metal case is that the d-s interaction energy must separately be calculated by using an appropriate model for the d-electron density.

2.3 THE CALCULATION OF THE TOTAL ENERGY

To obtain the total energy /2.10/, E^o_{ds} and E_d as defined by /2.12/ have still to be calculated. For the atomic-like d-functions needed in

$\rho_d^o(\underline{r}\underline{r}')$ a conveniently simple analytic representation [26], [27] is

$$\psi_\lambda(\underline{r},\alpha) = R_2(r,\alpha_i A_i)\cdot\psi_{2\lambda}(\Theta\varphi) \qquad \lambda=-2,\ldots,2 \qquad /2.19/$$

with the radial part consisting of the combination of two Slater-type orbitals /STO/

$$R_2(r,\alpha_i A_i) = A_1\left(\frac{(2\alpha_1)^7}{6!}\right)^{1/2} r^2 e^{-\alpha_1 r} + A_2\left(\frac{(2\alpha_2)^7}{6!}\right)^{1/2} r^2 e^{\alpha_2 r} \qquad /2.20/$$

This approximation was seen to work reasonably for free atoms and ions of transition elements, there was a reason therefore to use them for the metallic case with the parameters to be varied.
Clearly, T_d^o and the exchange parts of E_{cd}^o and E_{dd}^o, as calculated from the non-diagonal elements of $\rho_d^o(\underline{r}\underline{r}')$ depend only implicitly on R_a, as far as the parameters in the wavefunction which minimize the total energy vary with the atomic radius. The explicit R_a - dependence of the kinetic and exchange energy of d-electrons arises through the terms coming from $\rho_d^{ov}(\underline{r}\underline{r}')$ and is thus included in the S^2 -energy E_d^S. In the exchange charge approximation [18], [12] one has

$$E_d^S = c\cdot\left[S(R_a)\right]^2/R_a \qquad /2.21/$$

where c is a constant and the 'effective' overlap integral /standing, for simplicity, for all three kind of overlap parameters arising from the angular dependence of /2.19// is defined by

$$S(R_a) = \int_0^\infty R_2(r)\, R_2(|\underline{r}-\underline{R}_{nn}|)\, r^2\, dr \qquad /2.22/$$

where $\underline{R}_{nn}$ is the coordinate of the nearest neighbour ion. It is to be pointed out that, in contrast to the original treatments [18], [28], where E_d^s is assumed to contain <u>all</u> effects of the overlap between d-shells, here the proper coulomb contributions of E_{cd}^o and E_{dd}^o are treated separately without restriction to the S^2 - approximation. Incidentally, this does not invalidate the arguments leading to the form /2.21/, only the meaning of the coefficient C changes. In fact, the interatomic coulomb terms being attractive, the energy expressed by E_d^S must, in the present case, to be much more repulsive.
Instead of trying to estimate C from calculations of different two-centre integral [28], presently it is left to be a free parameter which should, alike r_i^2, be determined from the lattice equilibrium conditions.
For the coulomb terms in E_{cd}^o, E_{dd}^o and E_{ds}^o <u>one need not resort to the S^2 -approximation</u>, due to certain 'a priori' knowledge of the actual charge distribution.

Such is, first of all that the total charge contained in the atomic cell is fixed,

$$\int_{WS} \tilde{\rho}_d(r) r^2 \, dr = z - l \qquad /2.23/$$

and also that the density is smooth at the boundary,

$$\left(\frac{d\tilde{\rho}_d}{dr}\right)_{r=R_a} = 0 \qquad /2.24/$$

For the concrete shape of the d-density the construction of Stern [17] was adopted, which completes the atomic-like part of the density by adding a polinomial,

$$\tilde{\rho}_d(r) = \begin{cases} \rho_d^o(r) + \sum_{k=o}^{2} c_{2k}(R_a)\, r^{2k} & r \leq R_a \\ 0 & r > R_a \end{cases} \qquad /2.25/$$

The general requirements /2.23/ - /2.24/ determine two of the c_{2k}, while for a third condition one of the followings were used,

a/ the d-density goes to zero at the origin, yielding $C_o = 0$

b/ C_o is determined as the density produced by neighbouring atoms with the densities corresponding to the wavefunction /2.19/ - 2.20/.

While the second condition implies superposed atomic densities, which is the usual starting form for the density in band structure calculations, the first reflects the fact that a Wigner-Seitz solution of the Schrödinger equation leads to zero charge at the origin. Both conditions were tested here, in order to check the sensitivity of the final results upon the choice of $\tilde{\rho}_d$. It was found that neither the use of b/ instead of a/ or the degree of the polinomial is substantial, the total energy is rather insensitive to further refinements of $\tilde{\rho}_d$.

Using then /2.25/ for the d-electron density, together with the OPW representation for the s-electrons, it is straightforward to obtain analytic expressions for all coulomb terms in E^o_{dd}, E^o_{ds} and E^o_{cd} which are, in fact, combinations of exponential and polinomial terms[+].

The quantity E^o_{ds} represents the screening by d-electrons as seen from the OPW band and its effect will be seen in figs. 2,4 and 6 in the next section. The present calculation for E_d gives /fig.2./ a shape substantially differing from the familiar form of a simple monotonic repulsion. This result, which proves to be essential in the final interpretation, can be obtained by avoiding the S^2 approximation for the coulomb terms and using

[+]To calculate E^o_{cd}, inner core orbitals are also needed. These were taken in the same analytic form as for free atoms [26], [27].

the closed scheme of calculation described above. It may be noticed that the result does not imply that forces between two closed shell atoms are not repulsive, since the definition of E_d contains the plus charge in the ion binding the OPW s-electrons, which does not arise in the case of, say, two helium atoms.[++]

2.4 NUMERICAL RESULTS

Having calculated each term in the total energy /2.10/ - /2.12/, it remains to fix both the variational parameters $(\alpha_i A_i)$ in the wavefunction and the constants r_i^2 and c. This, in principle, is not straightforward, since the variational parameters can be determined only when r_i^2 and c are already known. The first step can be to fix $(A_i \alpha_i)$ near to their atomic values and fit r_i^2 and c by use of the lattice equilibrium data, then find the new, say, A_2 value by minimizing the total energy. It turns out, however, that no new steps are indeed necessary, since the repeated fit of r_i^2 and c and the next value of A_2 do not differ appreciably from the result of the first step. In the present calculation only A_2 was varied, fixing α_1, α_2 at the atomic values obtained by a heuristic fit to Hermann-Skillman tables [26]. The reason for this is that by allowing all three parameters of the two-STO d-orbital to vary, the resulting 'best' wavefunction in the Hartree-Fock sense will not be the 'best' in the 'overlap' sense, namely it will fall off too quickly with distance leading to unrealistically small overlap integrals [27]. To avoid this difficulty was only A_2 taken to vary, but even this freedom gives valuable information on the change in shape of the wavefunction, when going from atomic to crystalline state[+]. As a result, at the values α_1=5,06 a.u. and a_2 = 1,80 a.u. the total energy for the atom is minimum at A_2^{at} = 0,4494, while this number for the metal is A_2 = 0,4540. The effective d-orbitals move thus outward from the ion, and though the effect is small, it shows the expected trend. Incidentally, the further tendency of spreading out of the d-orbitals is counterbalanced by the increase of the S^2 -term with increasing A_2/A_1. To check the adequacy of both the approximate wavefunctions and the use of the effective overlap S, the function $S^2(R_a)$ was fitted to an exponential near the equilibrium atomic radius as

$$S^2(R_a) \sim \exp(-R_{nn}/\rho) \qquad /2.26/$$

and the value ρ = 0,2805 Å was found, comparing well with the accurate atomic result by Hafemeister [12], 0.2777 Å.
In fig. 1. the fitting of the two parameters r_i and c is shown, using the lattice equilibrium data R_a = 2,66 a.u. and B = 1,420 Mbar [30]. The intersection of the two curves gives r_i = 1.2852 a.u., C = 289.3 a.u.
The importance of the result for r_i becomes evident, if one realizes that

[+] To obtain this trend was also one of the goals of the calculation by Lundqvist [29].

[++] Similar behaviour was found by Schneiderman et al. [34] in the case of $He\text{-}Li^+$ system.

the above value, which is determined from lattice dynamical data, compares fairly well with the 'ab initio' estimate for the core radius r_c defined by /2.15/, this being 1.2695 a.u. The near equality of these two numbers indicate that the meaning of r_i can be maintained, even for noble metals, as an Ashcroft radius, determined essentially by inner core orbitals of the same symmetry, as in the case of non-transition metals.
The result for c can be made more familiar if one fits [18] E_d^S to a Born-Mayer function around the equilibrium volume,

$$E_d^S = c\left[S(R_a)\right]^2/R_a \approx D\, e^{-(R_{nn}-R_{nn}^o)/\rho_1} \qquad /2.27/$$

where R_{nn}^o is the equilibrium nearest neighbour distance. For the constant determining the R_a-dependence of E_d^S the value $\rho_1 = 0{,}2525\text{Å}$ was found, again near to that found by using atomic wavefunctions [12] $\rho_s^{at} = 0{,}25\text{Å}$ which could be expected already on the base of the agreement for ρ in /2.26/, and showing again the adequacy of using the 2-STO form for d-orbitals and the 'effective' overlap approximation. The value D/6, in turn, may be compared to the usual Born-Mayer amplitudes of pair interaction, as by definiton E_d^S is the contribution for unit cell. One has D/6 = 0.3376 eV which is 2-3 times as large as the values quoted, for example, in the work [2]. This is, of course, not surprising, since here the account for the exchange charge terms is made without the attractive coulomb terms which, according to Dick and Overhauser's work [18] reduce the amplitude of E_d^S by about a factor of two. In the present calculations the equilibrium bulk modulus was calculated as

$$B = \frac{1}{12\pi R_a}\,\frac{d^2E}{dR_a^2} \qquad /2.28/$$

and the dependence of A_2 on R_a was neglected, although in principle this contributes to B also. This dependence is, however, rather weak, as a consequence of the balance between effects favoring and acting against large overlap, as discussed above, thus the resulting contribution to B is less than 2 per cent which is negligible in the present calculation. The main results of the paper are shown in fig 2. and in table 1. In fig 2. the total energy E is plotted as a function of R_a, and the contributions E_s and E_d are also shown. Discussing first the s-energy contribution $E_s(R_a)$, it is seen to show a similar behaviour as Fuchs' 'ab initio' Wigner-Seitz results. It is noticeable, as seen from the shape of $E_s(R_a)$, that a reasonable estimate for the atomic radius and cohesive energy may be obtained by taking into account solely this part of the total energy. The reason why the s-energy alone would produce the observed small value of Wigner-Seitz radius can be explained as follows. During the process of filling the d-shell from potassium to copper, the OPW core radius is progressively decreasing, as the 3 s shell is pulled more and more inward to the nucleus. This is shown in fig 3. for the 3-d transition series. /In calculating OPW radii r_c, the d^nS

configuration was assumed for each element and a modified STO approximation [27] was used for inner orbitals. The orthogonalization was performed only with respect to the 3 s shell, which is sufficiently accurate here./ Assuming that r_i behaves similarly to r_c, which is certainly the case for both potassium and copper, where the available values for r_i are also shown in the figure, the minimum of $E_{s,b}$ is then progressively shifted toward smaller radii. In consequence, the position of the minimum of E_s is also moving inward and the effect is only enhanced by the monotonic increase of $\lambda_o z_{eff}$ /see fig. 4/ for smaller radii. Incidentally, the substantial role of s-electrons in adjusting the equilibrium atomic radius is suggested already by the fact that the ration r_c/R_a, plotted also in fig. 3., has appraximately same constant value for copper and potassium, and that the definition of r_c /2.15/ is by no means related to d-orbitals. This is not the case, of course, for transition metals having incomplete d-shells, where the non-vanishing d-band contribution causes the characteristic atomic number dependence of the Wigner-Seitz radius [13], in contrast with this monotonically decreasing behaviour.
Since, on the other hand, the bulk modulus obtainable only on the base of E_s is much less than that observed, this has led first Fuchs [1] and later others [2], [3] to add to it a term representing repulsive core-core interaction. Such repulsion, often parametrized as a Born-Mayer potential, makes it surely possible to find a convenient bulk modulus, but to keep the minimum of the total energy at the observed atomic radius one has, in turn, to distort the $E_s(R_a)$ curve. This is clear even from an inspection of Fuchs' fig 3, [1] or it has been made explicit by the negativ value for r_i^2 found by Jaswal and Girifalco [2]. In the present model, as a consequence of separating out the coulomb type overlap effects from the total exchange-charge interaction and treating them by a spherical model, the d-electron energy in /2.12/ is no more a monotonic function, and it comes out to be slightly attractive at lattice equilibrium, both its value and contribution to the pressure being negative. The d-energy E_d is, in fact, near to its minimum close to $R_a=2.66$ a.u. having a considerable positive curvature which contributes to the bulk modulus. In table 1. the contributions to the energy, pressure and bulk modulus are summarized. In the energy values, the quantities denoted by (at) are those calculated for the atoms with the quoted $(\alpha_i A_i)$ values. It is seen how the positive pressure of E_d^S is slightly overcompensated by the coulomb terms in E_d. The s-electron value of the bulk modulus, as calculated by /2.28/ is larger than Fuchs' result, mainly as a consequence of the introduction of λ_o to the band kinetic energy, since the curvature of $E_{s,b}$ is, in accordance with Fuchs' prediction, rather small. Some check of the calculation is offered by the total energy and the derivative of the bulk modulus vs. pressure in table 1. In view of the large scatter between different data for this latter, the theoretical values can be regarded as reasonable. It is noticeable that the value for $E_s+I=-0.160$ ry

is again very close to the value of Fuchs, and that a negative value of $E_d - E_d^{at}$ is needed to come nearer to the observed cohesive energy -0.257. /For the ionization energy I=0.5677 ry was used./ Incidentally, these results seem to support an essential approximation of a previous work [13]. In that paper the effect of d-electrons in the total energy was taken as merely the band-structure contribution for the general case of transition metals, wich becomes zero for copper. In fig. 2. one can see why this approximation is not too bad for the calculation of the atomic radius and cohesion energy, and why it leads to large error for the bulk modulus. The shape of the s-electron energy used in that previous paper was similar to that found presently, although the 'bottom of band' was defined by a formula like /2.18/ with a constant z^* insteed of $\lambda_o z_{eff}(R_a)$. To check the approximate adequacy of such an approach, in fig. 4. z_{eff} and $\lambda_o z_{eff}$ are plotted as a function of Ra . One can see that, in a model neglecting the R_a dependence of λ_o, the resulting effective charge, which accounts already for the incomplete screening by d-electrons, is remarkably constant, having the value in the present model as $z_{eff}(R_a = 2{,}66) = 1{,}135$. The introduction of the orthogonality hole through λ_o modifies somewhat the picture, increasing ultimately $\lambda_o z_{eff}$ for decreasing R_a . As a further check of the results, the equation of state for copper is shown in fig. 5., together with the experimental values by Keeler and Kennedy [31] and Altsuler et al. [32]. The two theoretical curves correspond to the slightly different model assumptions for the d-density rearrangement, as discussed in connection with /2.25/. This example illustrates incidentally the fact that the results are actually not very sensitive to the actual shape of the polinomial density, defined in /2.25/, provided /2.23/ and /2.24/ are fulfilled. The theoretical curve goes slightly higher than the experimental, the agreement being, however, not too bad.

Finally, the model implies some predictions on the variation of the 'average band structure' with lattice spacing. Besides the bottom of the band E_{sb} , the average s-energy E_s , and the model Fermi-energy $E_F = \lambda_o k_F^2$ one can also see to what extent the more effective screening, as compared to the atomic case, by both the s and d electrons shifts upward the average d energy or 'centre of gravity' of the d-band $E_{d,g}$. This shift, due solely to that in the potential energy of d-electrons, is shown in fig.6. together with E_F E_s, and E_{sb} . For this latter, some band structure results for the equilibrium lattice spacing are also shown, besides the quoted results by Fuchs [1]. One can see that, despite of the very crude approximations from the point of view of band structure theory, the average energies and their variation with the atomic radius are not unreasonable. The different estimates, for example, of the position of the bottom of s-band scatter around the present value. As to the average d and s energies, these are nearly equal at $R_a = 2{,}66$ a.u. The difference $E_{d,g} - E_{sb} \sim 0{,}35$ry is coherent with the values $E(\Gamma_{25'}) - E(\Gamma_1)$ obtained by band structure methods [33]. The

renormalization shift for $E_{d,g}$ as calculated by Watson et al [6] is more than twice as large as the present 0.19 ry, the difference being entirely due to the different techniques in calculating d-densities in the metal. This can be understood, since really slight differences in the shape of the d-density will change the position of $E_{d,g}$ considerably, in view of the large number of interacting d-electrons.

3. CONCLUSION

Instead of the usual Born-Mayer type repulsion, the interaction energy of the d-shells was found to be slightly attractive and have a minimum near the equilibrium atomic volume, and it becomes repulsive only at smaller Wigner-Seitz radii. Such complex behaviour of the d-type energy seems to have been indicated already by the results of Fuchs and other workers, and the neutral sphere model in its present generalized form explains it by treating the overlap coulomb terms separately from the other contributions of order S^2. Besides the reasonable agreement of the theoretical values for cohesive energy and the equation of state, the value of the Ashcroft radius r_i for the s-electrons is in remarkable coincidence with the 'ab initio' calculated OPW core radius r_c. In going from the atomic to metallic state, the atomic-like wavefunctions for d-orbitals tend to spread out, although the effect is restricted by the balance between variations of the attractive and repulsive terms in the total energy. The results seem to be useful in further calculations concerning other dynamical properties of the noble metals as shear constants and phonon frequencies on the one hand, and the volume dependent properties of transition elements with partly filled d-shells, on the other hand.

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FIGURE CAPTIONS

Fig.1. Fitting of the parameters from lattice equilibrium data. Besides the curves with R_a = 2.66 a.u. and B_o = 1.42 Mbar /Ref. 30/, the other pair of curves illustrate how much r_i^2 and C are affected by small changes in the equilibrium data.

Fig.2. Total energy vs. R_a for copper. Besides the total energy E, the contributions E_s and E_d defined by /2.11/ and /2.12/ respectively, are also plotted. E_c^{exp} is the observed cohesive energy equal to 0.257 ry, I = 0.5677 ry is the first ionization energy of the atom and E_d^{at} is the value of E_d for infinite R_a.

Fig.3. Dependence of the OPW core radius on atomic number for the iron group. In addition to r_c defined by /2.15/, the available values for r_i are also shown. For potassium one has, besides the crystallographic ionic radius r_i^C, the results by Ashcroft /J. Phys. C, 1, 232, 1968/ r_i^A and by Brovman et al. /Ref. 11/ r_i^B. For copper, the present result is r_i^{Cu} = 1.2852.

Fig.4. The average effective charge Z_{eff} vs. R_a. The quantity Z_{eff}, as defined by /2.17/ and /2.18/, contains the screening by d electrons.

Fig.5. Equation of state for copper. The experimental curves, denoted by x /Ref. 32/ and ⧗ /Ref. 31/ are compared with the theoretical results. For the calculation of c_o defined by /2.25/, two different approximations were used, as discussed in the text /in the case of the solid line c_o = 0/.

Fig.6. One-electron levels for copper vs. R_a. Besides the "average" electron levels E_S and $E_{d,g}$, the bottom of the s band $E_{s,b}$ and the Fermi level $\lambda_o k_F^2$ are also plotted. The Wigner-Seitz result by Fuchs [1] for the bottom of the s band is also shown. The points at the equilibrium atomic radius are the results of different band structure calculations for $E(\Gamma_1)$ for copper.

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TABLE CAPTION

Different contributions to the total energy (E), pressure (P), bulk modulus (B), and the pressure derivative of the bulk modulus $\left(\frac{dB}{dP}\right)$ for copper at the equilibrium atomic radius. The notations are the same as in the text.

	E[ry]	P[Mbar]	B[Mbar]	$\frac{dB}{dP}$
$E_{s,b}$	-1.101	-0.513	0.051	
E_d^S	0.149	0.934	3.052	
E_s+I	-0.160	0.050	0.757	
$E_d-E_d^{at}$	-0.035	-0.050	0.664	
$E-E^{at}$	-0.196	0	1.420	5.64
				5.59 [a]
				7,7 [b]
exp.	-0.257	0	1.420	4.1 [c]
				5.3 [d]

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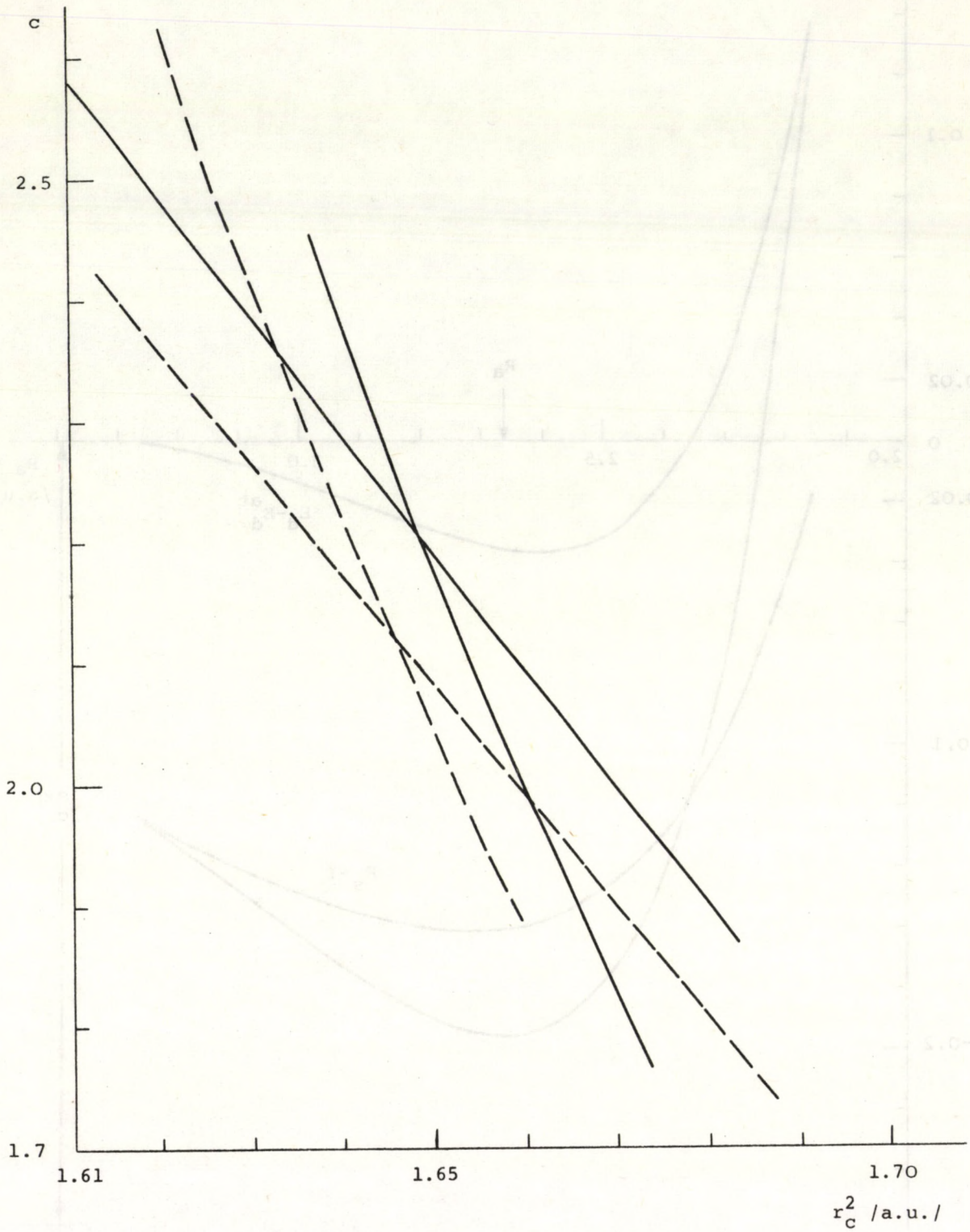

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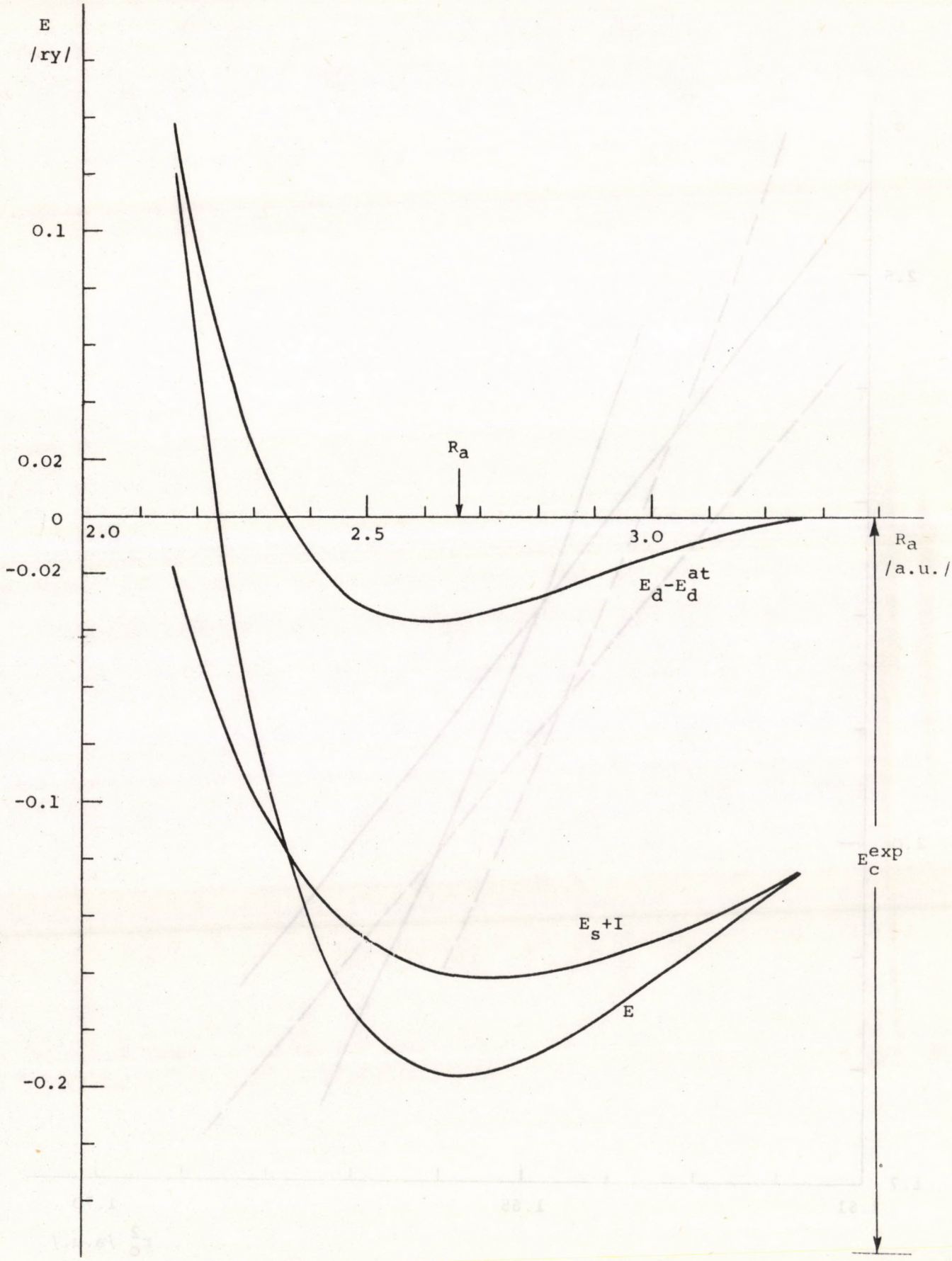

Fig. 2

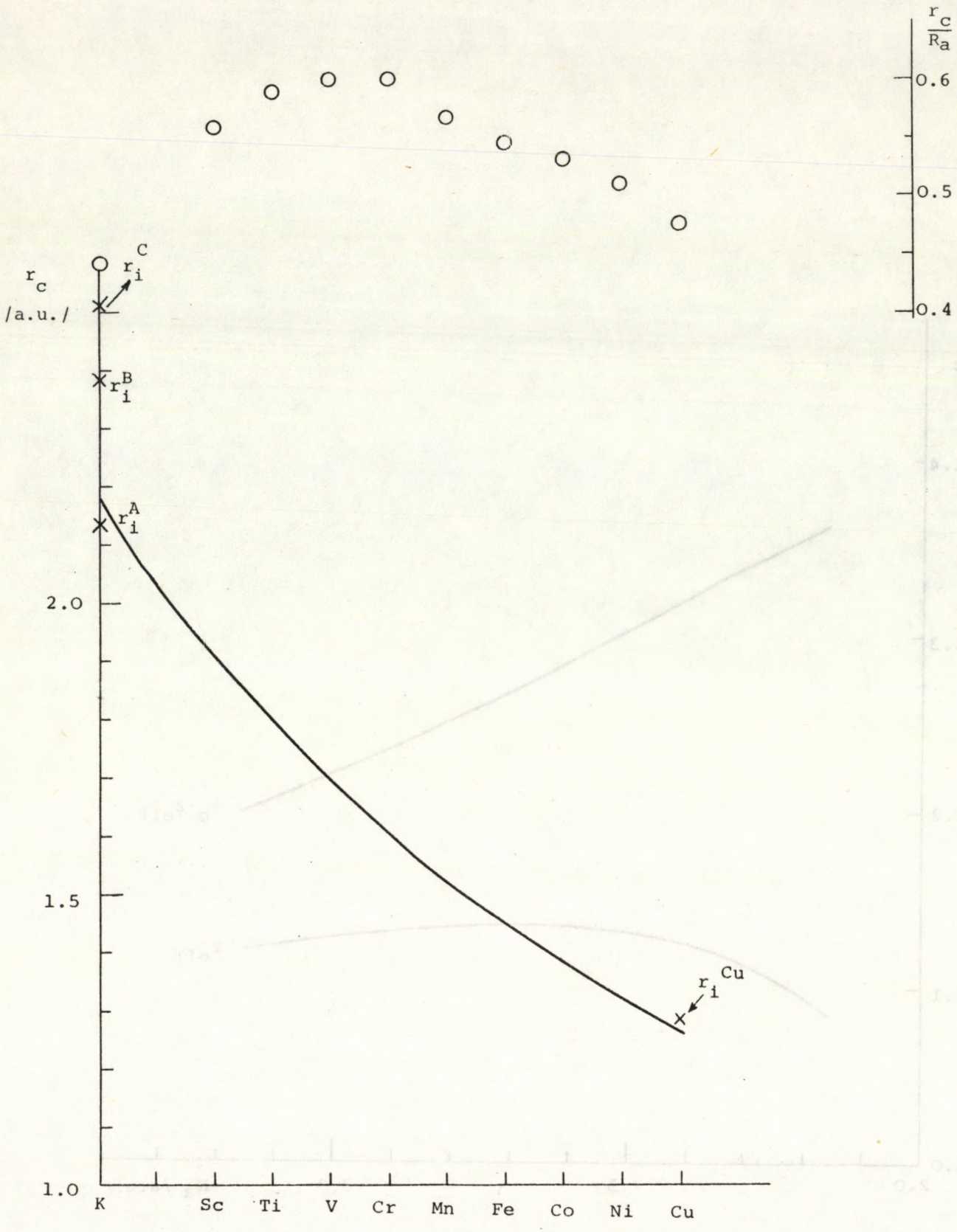
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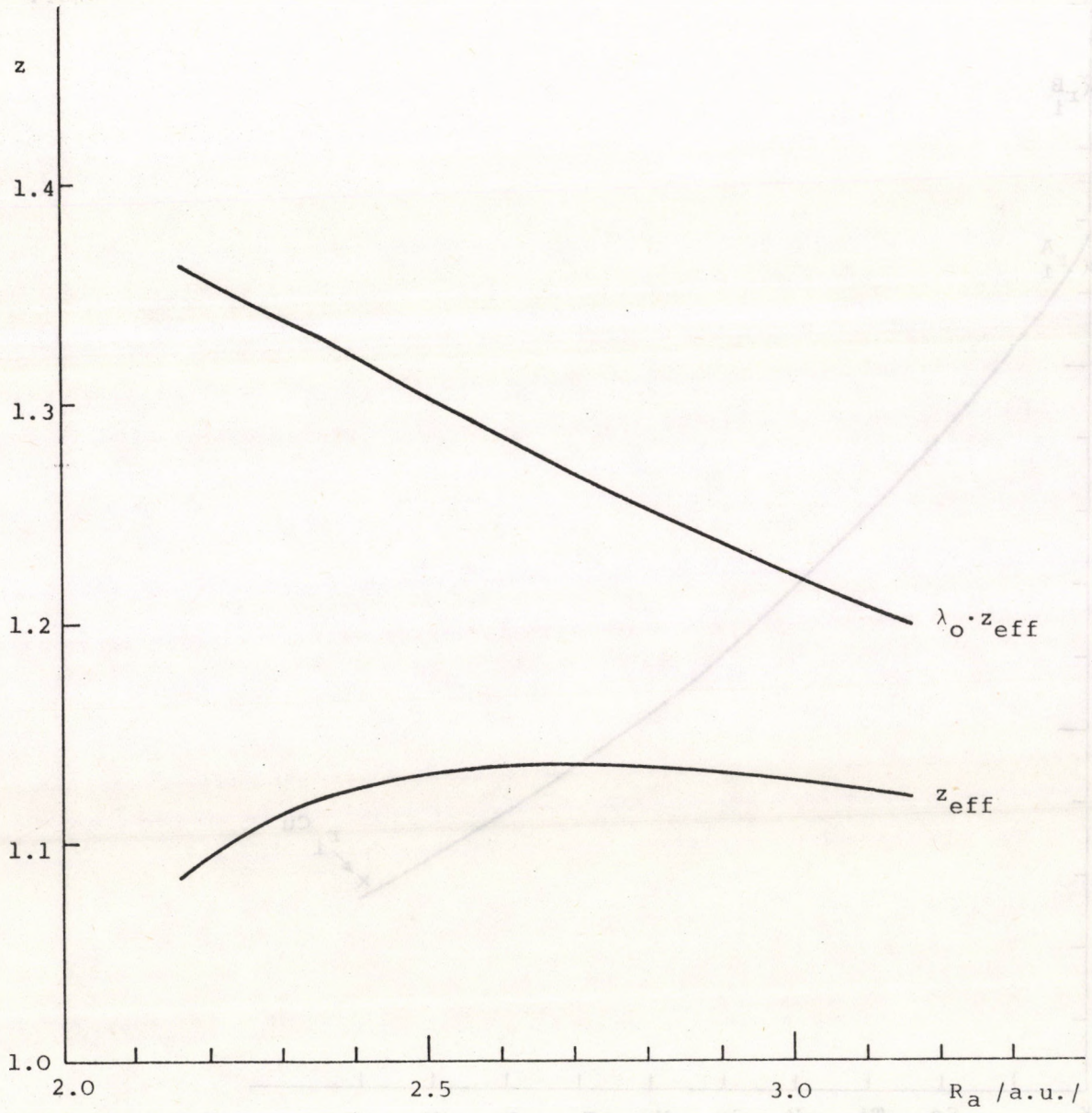
Fig. 3



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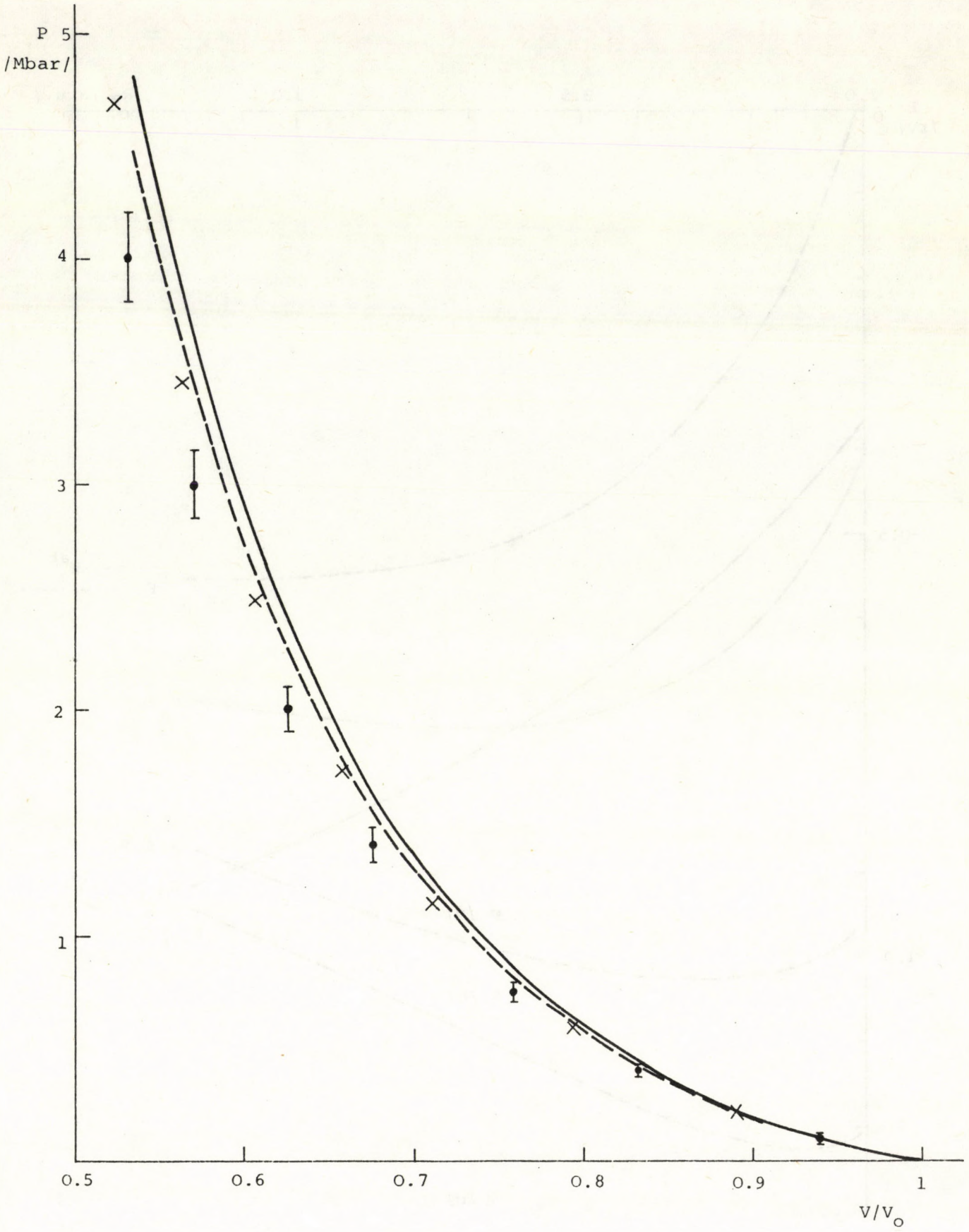

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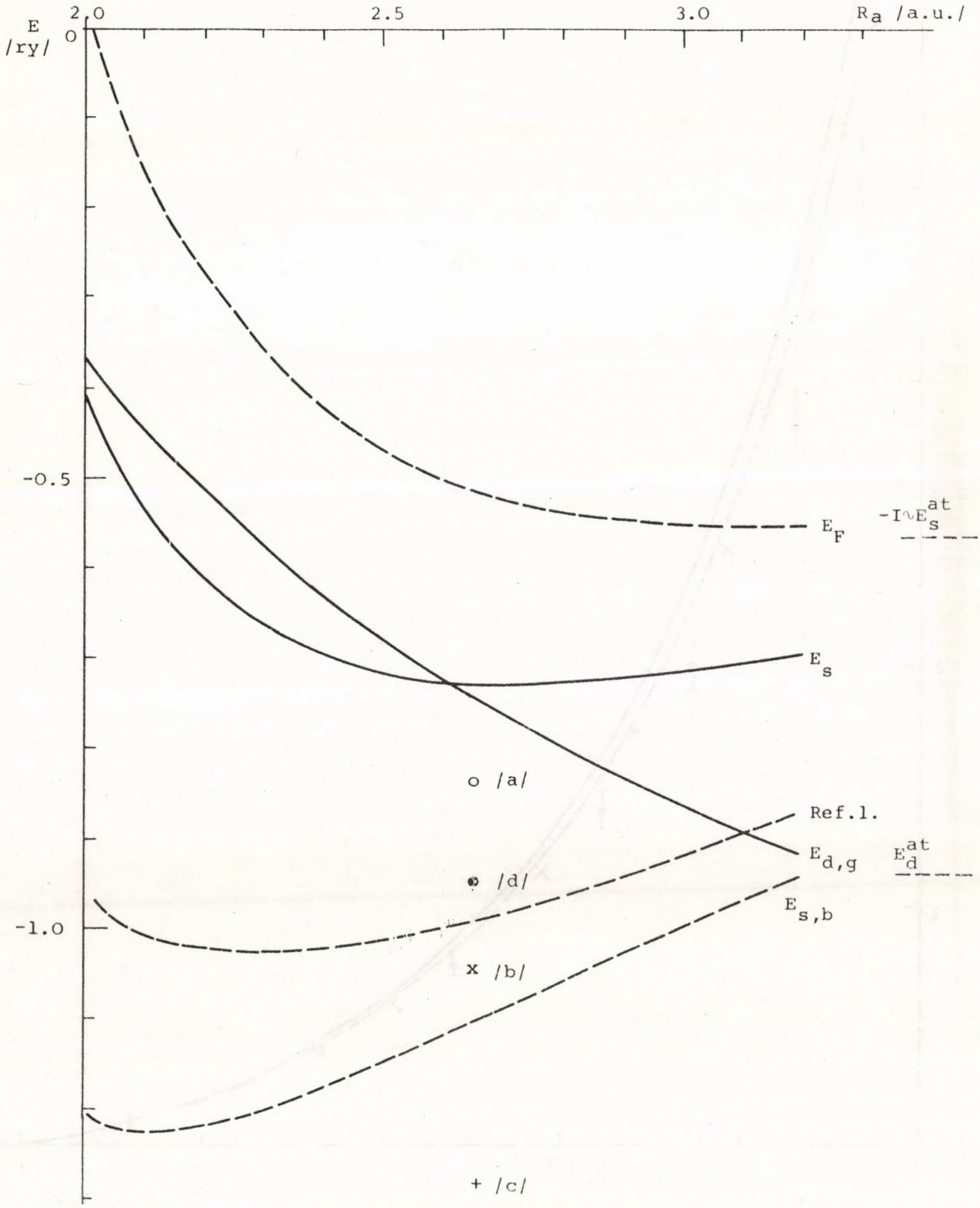
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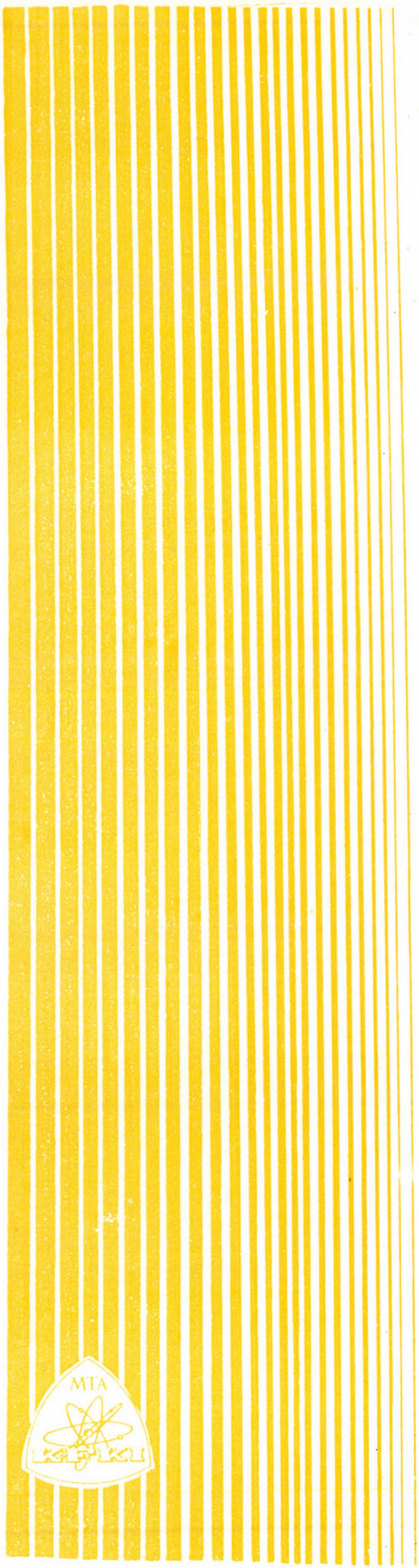
Fig. 6



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